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COMPATIBILITY, PROCESSABILITY AND CURE BEHAVIOR OF  
BENZIL END CAPPED ACETYLENE TERMINATED QUINOXALINE  
OLIGOMER WITH ACETYLENE TERMINATED PHENOXY DILUENT

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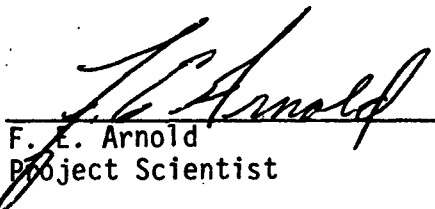
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This technical report has been reviewed and is approved for publication.

  
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Benzil end-capped acetylene terminated phenyl quinoxaline (BATQ-H) oligomer undergoes thermally initiated polymerization through its reactive acetylene groups. The cured resin is high temperature resistant and has a $T_g$ of 330°C. However, it is difficult to process due to its lack of necessary flow and has an insufficient "reaction window" for cure. To improve the processability, 10 and 20 weight percent of low molecular weight acetylene terminated phenoxy (ATP) is added to the BATQ-H and the blends were obtained by		

## 20. Abstract (Concluded)

freeze-drying. The 80 BATQ-H/20 ATP and 90 BATQ-H/10 ATP (ATP containing both the monomer and the oligomer) exhibit Tgs of 74 and 111°C, respectively. Cure-phase diagram of the BATQ-H/ATP blends show availability of sufficient time for processing before vitrification occurs, thus providing an expanded "reaction window."

Complex viscosities of BATQ-H and BATQ-H/ATP blends were determined isothermally on the Rheometrics instruments using parallel plates mode. The starting viscosity of BATQ-H is  $10^4 - 10^5$  poise at 190°C when measured at a frequency of 10 radians/sec and rise sharply at this temperature. Whereas the viscosities of 80/20 and 90/10 blends start at  $10^2$  poise and rise at a much slower rate, providing additional time before the oligomers become unprocessable due to high viscosities.

The dynamic shear moduli of 80 BATQ-H/20 ATP and 90 BATQ-H/10 ATP cured blends were determined by Torsion Impregnated Cloth Analysis (TICA) specimens. The data suggest 275°C as the upper limit for end-use temperature.

## FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419, "Nonmetallic and Composite Materials," Task No. 241904, Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F. E. Arnold as the Materials Laboratory Project Scientist. Co-authors were Dr. S. Sikka, University of Dayton Research Institute and Dr. I. J. Goldfarb, Materials Laboratory, (AFWAL/MLBP).

This report covers research conducted from June 1980 to February 1981.

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## SECTION I

### INTRODUCTION

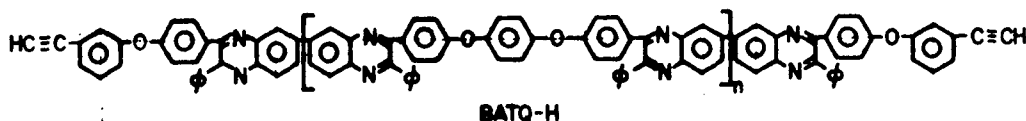
Benzil end-capped acetylene-terminated phenyl quinoxaline oligomer (BATQ-H) has been synthesized at the Materials Laboratory (Reference 1) to provide a high temperature resistant and moisture insensitive matrix resin (Reference 2). BATQ-H oligomer can be thermally homopolymerized between 200-250°C to form a crosslinked network structure which is stable at high temperatures and resistant to other environmental conditions. Preliminary studies (Reference 1) on BATQ-H show that it has a high glass transition temperature ( $T_g$ ) (150-170°C) as well as high cure-onset temperature (>170°C). Initial cure data (Reference 3) viz., viscosity vs. time, at 190 and 210°C display high initial viscosities which increase rather rapidly, limiting the necessary flow and time required for processing. Since BATQ-H has potentially good properties, methods have been sought to improve its processability. One approach to lowering the  $T_g$ , improving the flow behavior of BATQ-H and expanding the processing window is the addition of a low molecular weight, structurally similar, reactive diluent/plasticizer. The plasticizer selected for this study is the 1,3-bis-(3-ethynylphenoxy) benzene or in short: ATP (Acetylene Terminated Phenoxy). Since ATP has acetylene end-groups, it is expected to react with BATQ and/or thermally homopolymerize, forming a three-dimensional network structure as in other AT systems (Reference 4).

This report pertains to blending of BATQ-H with ATP and rheological studies of these blends in an effort to improve their processing parameters.

## SECTION II

### EXPERIMENTAL

The BATQ-H used in the present study has the following chemical structure and is from a scaled-up batch received from Gulf Research and Development Company.



The scaled-up batch was characterized by High Pressure Liquid Chromatography (HPLC) and showed some differences from the original BATQ-H synthesized at the Materials Laboratory. Therefore, the Gulf scaled-up batch of BATQ-H was purified for the present study by the following method.

#### 1. ANALYSIS AND PURIFICATION OF GULF BATQ-H

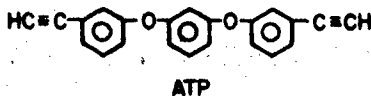
A 10 gram quantity of BATQ-H (from a 2 lb. batch supplied by Gulf Research and Development Company) was dissolved in 200 ml of chloroform and chromatographed on a column of silica gel. Early fractions eluted with chloroform afforded 0.65g of  $n=0$  component. Following this fraction was 0.17g of a material which was indicated by Thin Layer Chromatography (TLC) analysis to be a mixture of a small amount of  $n=0$  component with its characteristic blue fluorescence under short-wavelength ultraviolet light and a larger amount of a component with a dark appearance under the ultraviolet light. An infrared spectrum of this material showed an absorption at  $3620\text{ cm}^{-1}$ , possibly due to an N-H bond. Further elution of the column with chloroform afforded 8.97 g of material which appeared by TLC analysis to be BATQ-H with decreasing amounts of the  $n=1$ ,  $n=2$ ,  $n=3$ , and  $n=4$  components. Between each of the blue fluorescent spots corresponding to these components was a relatively small dark spot. After removal of all of the BATQ-H with chloroform, the dark material remaining at the top of the column was stripped with tetrahydrofuran to afford 0.48g of material whose TLC showed no fluorescent components and whose infrared spectrum showed a strong N-H absorption at  $3620\text{ cm}^{-1}$  and none of the  $\text{C}\equiv\text{C}$  absorption at  $3280\text{ cm}^{-1}$  which is characteristic of BATQ-H.

Unsuccessful attempts were made to separate the fluorescent BATQ-H components of the mixture from the dark impurities by the following methods: precipitation from chloroform solution by ethyl acetate extraction of either a chloroform or a THF solution with 20%  $\text{HBF}_4$  followed by neutralization of the  $\text{HBF}_4$  layer with  $\text{NH}_4\text{OH}$ .

Since the dark impurity eluted during chromatography with THF showed very little movement on a TLC strip when developed with ethyl acetate, it was decided that this material, amounting to  $\sim 5\%$  of the BATQ-H sample, could be removed by large-scale chromatography. A mixture of 3:1 chloroform: ethyl acetate was used due to the poor solubility of BATQ-H in ethyl acetate alone and the slow removal from a column with chloroform alone. A ratio of 1200g silica gel per 75g batch of crude BATQ-H was used for the columns. A solution of 75g BATQ-H in 750ml of chloroform was passed through filter paper to remove suspended insolubles before placing the filtrate on the column. Elution of each column was accomplished with 6 liters of 3:1 chloroform-ethyl acetate per 75g BATQ-H, at which point TLC analysis indicated very little BATQ-H still present in the eluate. All of the eluates obtained from a total of 575g of crude BATQ-H were distilled to near dryness, and the combined residues were taken up in 2 liters of chloroform and precipitated from 16 liters of methanol. After drying under vacuum at  $80^\circ$  overnight, 533g (92.6% recovery) was obtained.

## 2. ATP

Two different batches of ATP have been evaluated in the present study. One batch contains only the pure monomer of ATP (scaled-up batch from Midwest Research Institute) of the following chemical structure (Reference 5).



The second batch of ATP is the one synthesized at Materials Laboratory (Reference 3).

### 3. BLENDS OF BATQ-H/ATP

BATQ-H oligomer and ATP were weighed and dissolved in benzene. A 10% solution of 90 weight percent BATQ-H/10 weight percent ATP (90 BATQ-H/10 ATP) and 80 weight percent BATQ-H and 20 weight percent ATP (80 BATQ-H/20 ATP) were prepared. Four samples of BATQ-H/ATP blends were made. Two of these (90 BATQ-H/10 ATP, 80 BATQ/20 ATP) contain ATP monomer only while the other two blends contain ATP comprising mostly of monomer and oligomer.

The solution of these blends were frozen by immersing their containers in liquid nitrogen. The frozen blends were attached to the freeze-drying apparatus where benzene solvent was removed and the blends were freeze-dried for one week. Therefore the blends produced have a very large surface area and are expected to be homogeneous.

### 4. THERMOANALYTICAL DATA

The glass transition temperatures and cure-onset temperatures of BATQ-H oligomer, ATP diluent and freeze-dried BATQ-H/ATP blend, were determined on a Differential Scanning Calorimeter (DuPont Model 990).

### 5. DENSITY MEASUREMENTS

Density measurements of cured BATQ-H/ATP blends were determined by dropping small pieces of cured material in a density column filled with aqueous sodium bromide solution and calibrated with density floats of precisely known densities.

### 6. DETERMINATION OF CURE BEHAVIOR

#### a. Viscosities

The cure behavior of both the BATQ-H oligomer and BATQ-H/ATP blends was determined by measuring complex viscosities as a function of time, isothermally, on the Rheometrics Mechanical Spectrometer (RMS-7200). The freeze-dried material for which viscosities are to be measured were

pressed into pellets of 12mm diameter and 2mm thickness in a pellet-maker die at a pressure of 30,000 psi. In a series of runs, the pellets were placed on preheated parallel plates in RMS. The pellets were subjected to sinusoidal shear rate viscosity measurements at constant temperatures. In the present study, all viscosities were measured at a frequency of 10 radians/sec.

#### b. Vitrification Behavior

Vitrification behavior of BATQ-H and BATQ-H/ATP blends was determined on the Rheometrics Mechanical Spectrometer. The torsion-impregnated-cloth-analysis (TICA) specimens of uncured material were prepared as described in Reference 6 and cloth-resin composites in-phase and out-of-phase dynamic mechanical responses were measured isothermally as a function of time. The peaks associated with the vitrification of the resin occur in the glass-transition region and the time corresponding to the maximum of the out-of-phase component peak was taken as the time-to-vitrification or  $t_{vit}$ .

#### c. Tg Determination of Cured BATQ-H, BATQ-H/ATP

The glass transition temperatures of cured blends have been obtained on TICA samples. The TICA samples were first isothermally cured at 190°C and 210°C until the out-of-phase component shows a maximum, which is taken as the  $t_{vit}$ . Then the samples previously brought to vitrification were further cured isothermally under nitrogen in the environmental chamber of the RMS. The TICA samples were placed in the sample fixtures while temperature was raised at a rate of 12°C/5 secs interval up to the desired temperature. There is expected to be some temperature lag between the temperature read-out and the actual sample temperature. This lag is expected to be minimal. For example, for cure at 380°C, the time to attain the cure temperature is about 15 seconds as compared to cure time of 3600 seconds.

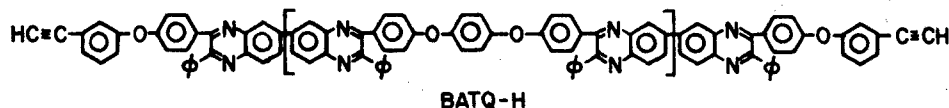
These TICA samples were held at 380°C for one hour and quenched by liquid nitrogen. The samples were then scanned up in temperature at a heating rate of 2°C/min and  $a'(G')$ ,  $b(G'')$ , and  $\tan \delta$  were plotted. The plots show the  $T_g$  of the blend. Once the scanning temperature went above  $T_g$ , the samples were scanned down at a cooling rate of 2°C/min to determine if any additional cure occurs in which case another  $T_g$  would be observable.

### SECTION III

## RESULTS AND DISCUSSION

### 1. CHARACTERIZATION OF BATQ-H

The BATQ-H oligomer used in the present study is a Gulf scaled-up batch and has been characterized by liquid chromatography to determine the various molecular weight species in it. Three different eluent peaks were detected. Their relative areas were determined to be 7.41, 50.75, and 41.84 percent. In terms of oligomer content 7.41% corresponds to  $n=0$ , 50.75% corresponds to  $n=1$ , and 41.84% to  $n \geq 2$  in the following structure.



In case of  $n=0$ , the species does not contain the moiety inside the bracket and the molecule is called "BA-DAB-BA" and has a molecular weight of 794g/mole. When  $n=1$ , the species is BATQ-H and has a molecular weight of 1462 g/mole. When  $n \geq 2$ , the molecular weight has not been calibrated and therefore it is difficult to breakdown the peak into individual molecular weight species.

The BATQ-H sample which has been purified as described earlier shows 7.1% corresponding to  $n=0$ , 49.9% corresponding to  $n=1$ , and 42.9% corresponding to  $n \geq 2$ . This indicates a small amount of BADABA and BATQ-H (monomer  $n=1$ ) is lost during the purification process as opposed to the higher molecular weight oligomer. However, all the impurities in BATQ-H have not been fully analyzed.

The Gulf scaled-up and purified batches of BATQ-H oligomer were characterized on the Rheometrics Mechanical Spectrometer in the parallel plate mode. Their complex viscosities vs. time at 190 and 210°C are shown in Figure 1. The data shown here are taken at 10 rad/sec. The viscosities of purified BATQ-H are somewhat lower than those of the unpurified Gulf scaled-up batch. This indicates that some of the higher molecular weight oligomers of BATQ-H may have been removed during the purification. These differences between the unpurified and purified

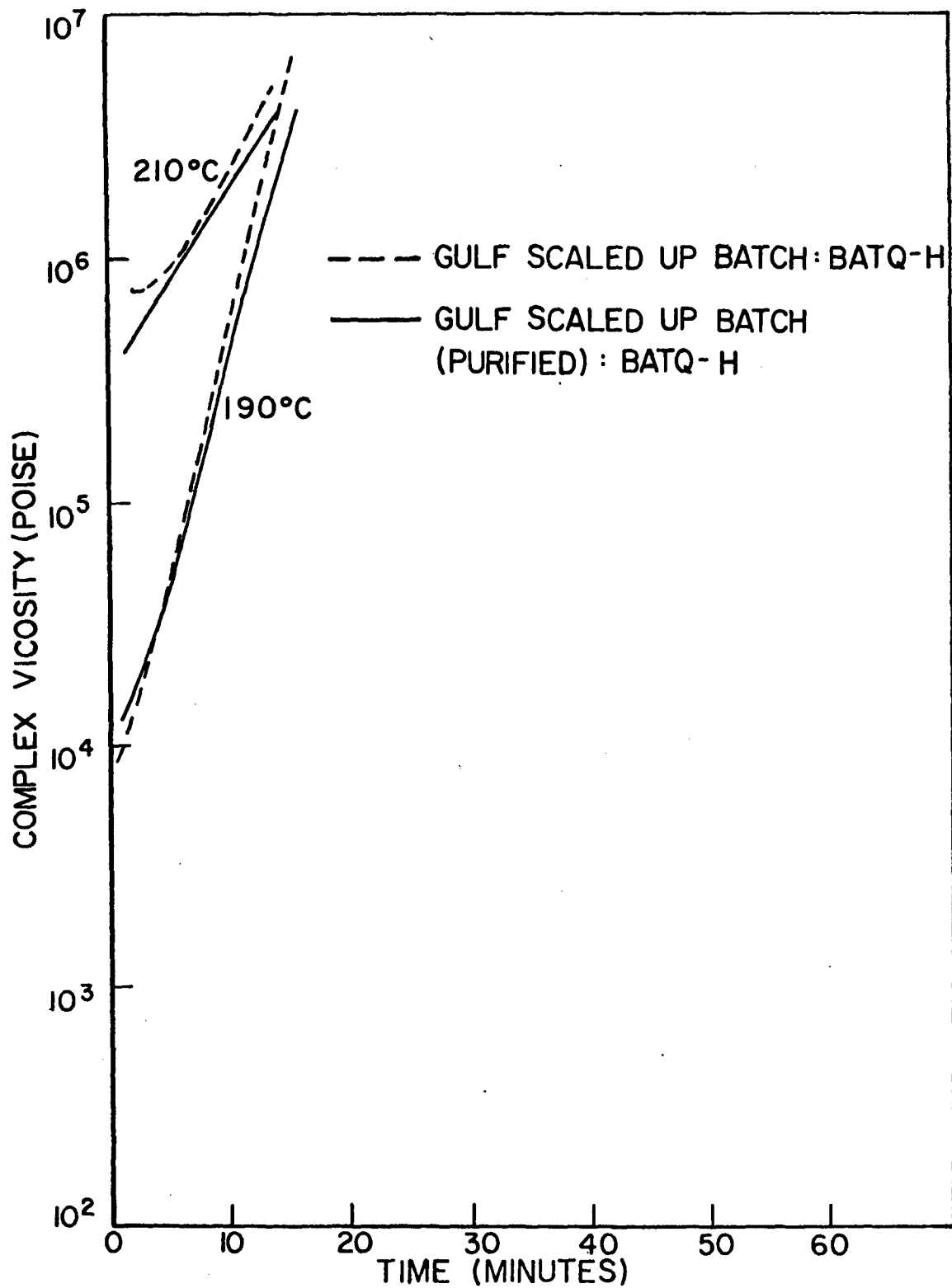


Figure 1. Viscosity vs. Time of BATQ (Gulf) and BATQ (Pure).



batches are also evidenced by DSC measurements. The Tg of Gulf scaled-up BATQ-H sample is 165°C as compared to a Tg of 154°C for the purified sample.

In the present study, data obtained are on blends of purified BATQ-H and ATP. In Figure 1, it is obvious that the complex viscosities of BATQ-H are  $10^4$  poise at 210°C and  $4 \times 10^5$  poise at 190°C during isothermal cures. The viscosities of BATQ-H rise steeply and within 15 minutes reach up to  $4 \times 10^6$  poise. Since the Tg of BATQ-H is 154°C, one has to cure the oligomers at temperatures greater than 154°C where it can flow. The oligomer has an onset of polymerization temperature of 170°C. Therefore, at 190°C and 210°C, cure proceeds rapidly without giving sufficient time for processing. These data will be discussed and compared with similar data obtained from BATQ-H/ATP blends.

## 2. CHARACTERIZATION OF BATQ-H/ATP BLENDS

Two different batches of ATP have been used to prepare blends of BATQ-H/ATP. One is ATP (containing monomer only) while the other shows five peaks in liquid chromatographic analysis, corresponding to 4.69, 19.62, 65.73, 4.96, and 4.97% area. The second, third and fourth peaks have been characterized to correspond with oligomer, monomer, and m-diethynyl benzene, respectively. Thermogravimetric Analyses (TGA) of freeze-dried blends of BATQ-H/ATP are obtained to determine the extent of residual solvent present in them. The 90 BATQ-H/10 ATP blend (containing ATP in monomer form only) shows 1% weight loss at 60°C due to solvent, 1% weight loss at 170°C (possibly due to sublimation of ATP), followed by a significant weight loss at 540°C due to thermal degradation. The 90 BATQ-H/10 ATP and 80 BATQ-H/20 ATP (containing monomer and oligomer) shows less than 0.5% residual solvent which is lost at <200°C. Another 1% weight is lost at >200°C possibly due to ATP sublimation followed by significant weight loss at 540°C due to degradation.

Thermal data of BATQ-H, ATP and their blends is shown in Table 1. The glass transition temperatures of BATQ-H, ATP, and BATQ-H/ATP are plotted in Figure 2. Blending of ATP in either form (monomer or mixture of monomer and oligomer) lowers the Tg of BATQ-H. The Tg of ATP (monomer) is -43°C and the Tg of ATP (monomer and oligomer) is -44°C. This can be

TABLE 1  
THERMOANALYTICAL DATA OF ATP, BATQ-H, AND BATQ-H/ATP BLENDS

COMPOSITION	OBSERVED T <sub>g</sub> (°C) (1)	CALCULATED T <sub>g</sub> (°C)	T <sub>poly</sub> (°C) ONSET	T <sub>poly</sub> (°C) PEAK	T <sub>g</sub> (°C) AFTER CURE(2)	TGA		
						TEMP	LOSS	COMPONENT
ATP (MONOMER)	-43		125	226				
ATP (MONOMER+OLIGOMER)	-44		135	228				
BATQ-H (GULF PURIFIED)	154		170	268	290			
90 BATQ-H/10ATP (MONOMER)	106	120	175	262	270	~ 60	1.0	SOLVENT (3)
						170	1.0	ATP
						540		BATQ-H
90 BATQ-H/10ATP (MONO+OLIG)	111	119	170	265	275	<200	0.5	SOLVENT (3)
						>200	1.0	ATP
						540		BATQ-H
80 BATQ-H/20ATP (MONOMER)	65	91	155	260	270	60	0.5	SOLVENT (3)
						170	2.0	ATP
						540		BATQ-H
80 BATQ-H/20ATP (MONO+OLIG)	74	91	170	260	270			

(1) T<sub>g</sub> determined by DSC @ heating rate of 10°C/min.

(2) T<sub>g</sub> determined by DSC @ heating rate of 10°C/min. after heating the sample up to 450°C

(3) Degradation of BATQ-H

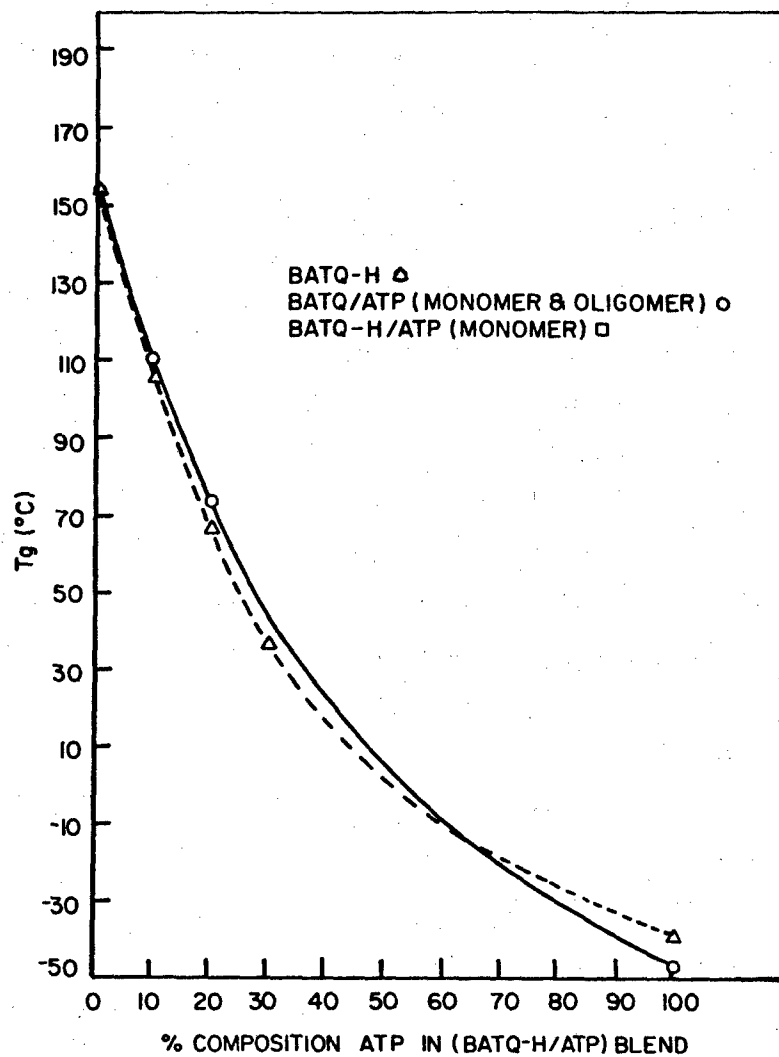


Figure 2. Plot of Observed  $T_g$ 's of BATQ-H, ATP, and Blends as Determined by DSC.

explained on the basis that ATP (monomer + oligomer) contains at least two components, 4.69 and 4.97% which have not been identified. One may be the solvent and the other diethynylbenzene. ATP (monomer) has not been characterized on the LC. Therefore, presence of any amount of solvent in ATP (monomer + oligomer) will lower its  $T_g$  as compared to ATP (monomer). However, when BATQ-H and ATP are blended together via freeze-drying, some of this solvent present in ATP (monomer + oligomer) is removed in the process. This would cause  $T_g$ 's of blends containing ATP with oligomer to be higher as opposed to ATP with monomer only. The calculated  $T_g$ s shown in Table 1 are arrived at by using the empirical equation  $1/T_g = W_1/T_{g1} + W_2/T_{g2}$ , where  $T_g$ ,  $T_{g1}$ , and  $T_{g2}$  are the  $T_g$ 's of blend, Component I and Component II respectively.  $W_1$  and  $W_2$  are the weight fractions of Component I and II, respectively. These calculated  $T_g$ 's are higher in all cases than the observed  $T_g$ 's. This has been usually the case when this empirical relationship applicable to copolymers has been applied to the oligomers. It may be pointed out that when there is solvent in any one of the components, the actual weight fraction of each component would vary somewhat from the originally prepared ratios.

The cure-onset temperature for ATP is 150°C and that of BATQ-H is 170°C. The cure-onset temperature or  $T_{poly}$  for blends is 170-175°C with the exception of 80 BATQ-H/20 ATP (monomer) blend. The  $T_{poly}$  is the temperature where the blends begin to react/crosslink reaching their peak at 260-265°C range. All the temperatures reported in Table 1 are obtained on Differential Scanning Calorimeter (DSC) at a heating rate of 10°C/min. The  $T_g$ 's of blends after heating them to 450°C, quenching and rescanning are found in the range of 270-275°C. Of course,  $T_g$ 's thus obtained may not be  $T_g^\infty$  since they were not cured at 450°C for any length of time to "fully cure" them. The time-temperature relationship for cure of blends is discussed in the following section on cure-kinetics data obtained on DSC.

### 3. CURE-KINETICS

Since the object of blending ATP with BATQ-H is to improve the processing parameters, cure kinetics plots have been obtained for BATQ-H, ATP, and their blends. A composite plot showing processing windows for their materials is shown in Figure 3. Though the plot shows temperatures

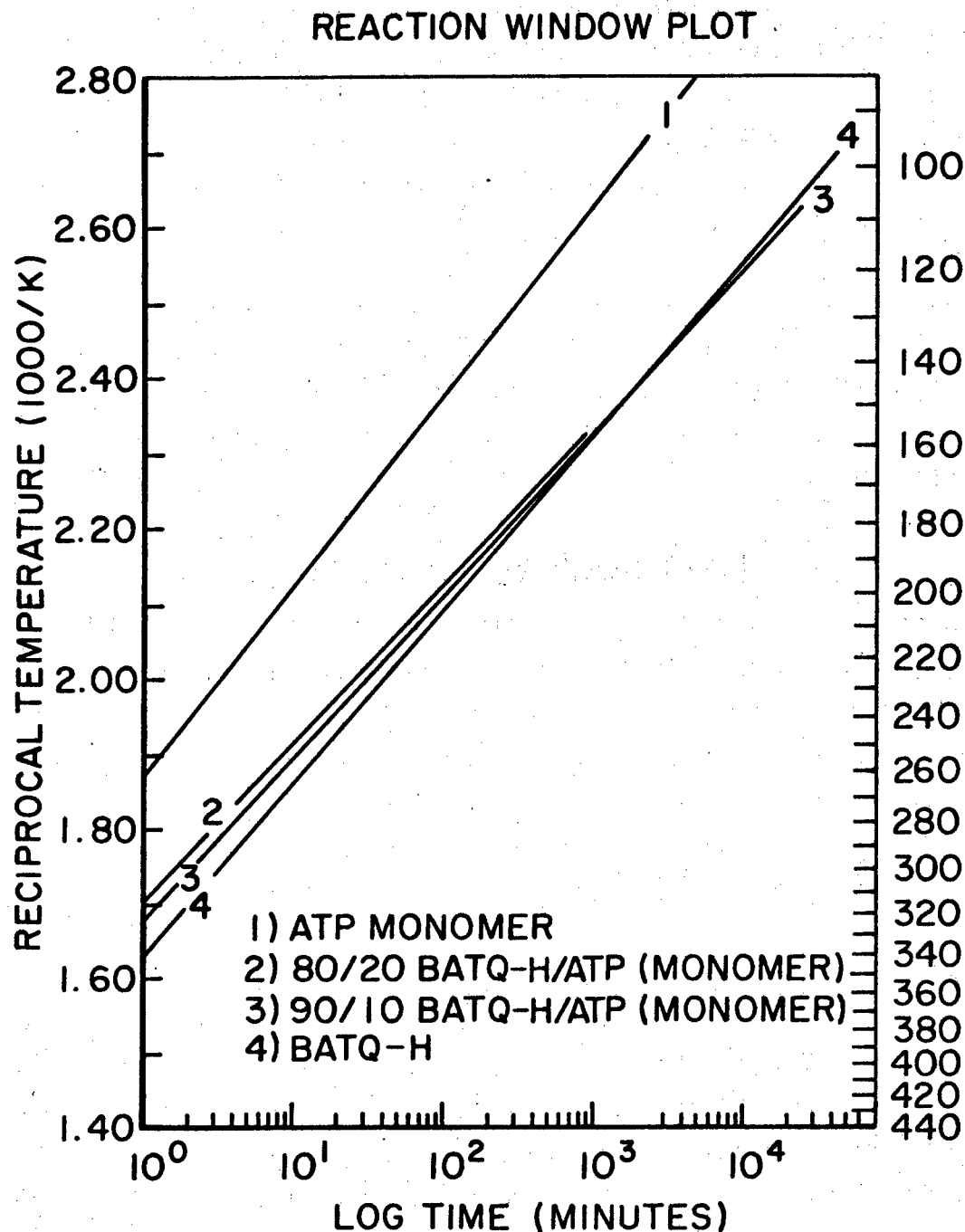


Figure 3. Reaction Window Plot of BATQ-H, ATP (Monomer), 90 BATQ-H/10 ATP (Monomer), and 80 BATQ-H/20 ATP (Monomer) for 95% Cure.

scaled from 100°C to 440°C, significant cure results are above the  $T_{poly}$  of oligomers listed in Table 1. It can be seen in Figure 3 that 90 BATQ-H/10 ATP and 80 BATQ-H/20 ATP blends can be cured at lower temperatures than BATQ-H if processing time is held constant or conversely the blends can be cured to the same degree (viz., 95% cure) by processing them for lesser time (than BATQ-H) while the processing temperature is kept constant. However, it is assumed that the polymerization/reaction is not affected by increased viscosity.

Figure 4 shows a composite cure kinetics plot for BATQ-H, ATP (monomer + oligomer), and 90 BATQ-H/10 ATP (monomer + oligomer). Again, the blends can be processed at lower temperature and/or for longer time than the BATQ-H oligomer by itself, depending on which parameter is held constant.

The cure kinetics data for various oligomers and blends are listed in Table 3. The table shows the activation energies, and heat of reaction in cal/g, respectively. The heat of reaction is given in units of cal/g because the molecular weights of their oligomers are not precisely known. However, if we assume that ATP (containing monomer only) does not contain any impurities and/or solvent, its molecular weight is 310g/mole. Using this molecular weight, the heat of reaction of ATP (monomer only) comes out to be 66.65 kcal/mole, which is very close to the heat of reaction found for various acetylene terminated systems. Assuming that the heat reaction (kcal/mole) is about the same for oligomers and blends of acetylene terminated oligomers, it is possible to calculate the number average molecular weight by knowing the heat of reaction in cal/g. The molecular weights of oligomers thus calculated are shown in Table 2. The number average molecular weight of BATQ-H is 1546 g/mole as compared to 1605 g/mole calculated by adding molecular weights of the fractions determined from LC data. The average molecular weight of ATP (containing both monomer and oligomer) calculates out to be 343 g/mole by the above method which is quite in agreement with its known composition and effect on  $T_g$  of the blends as shown in Table 1. The average molecular weights of blends prepared from ATP with oligomer are higher than the molecular weights of blends with ATP (monomer).

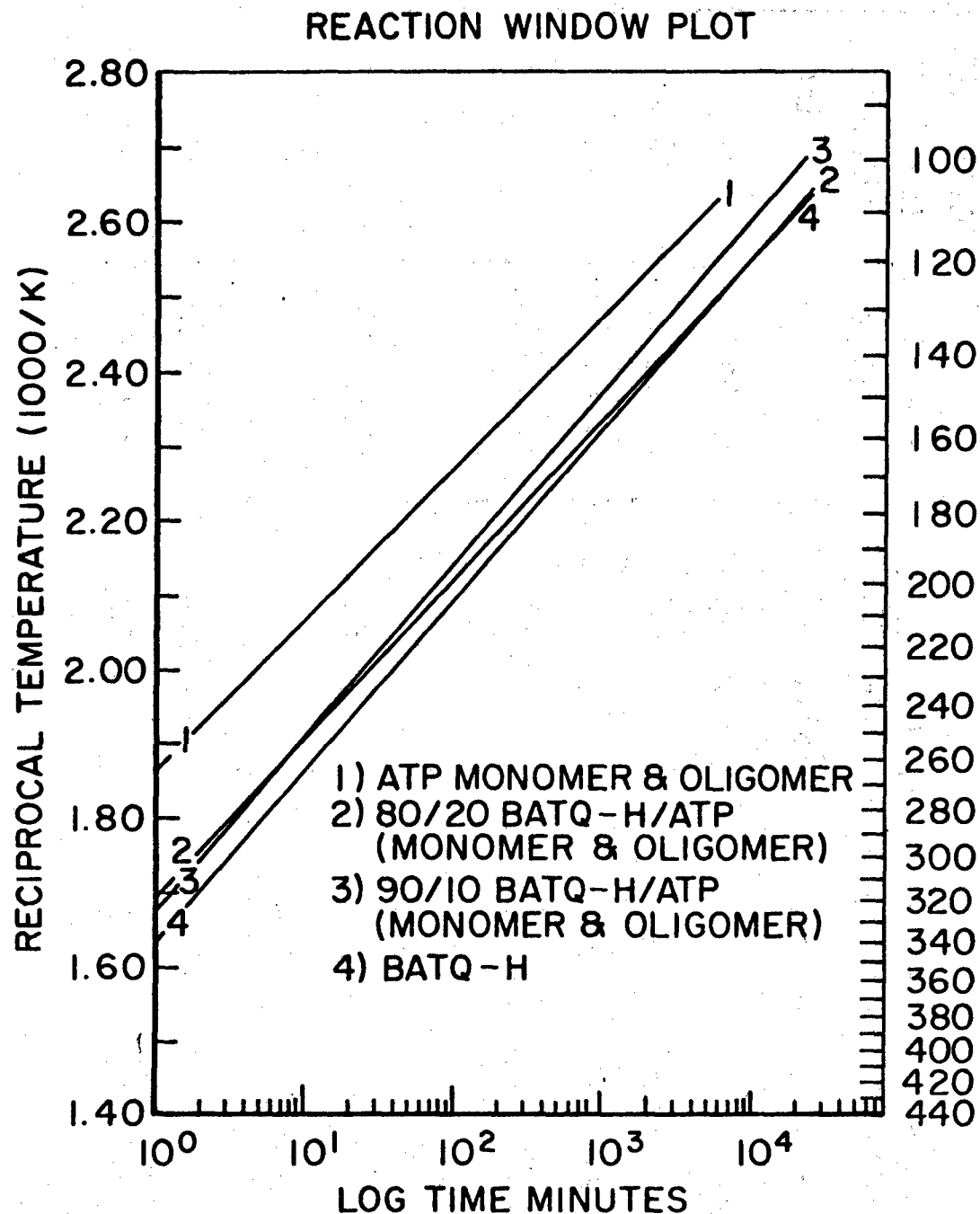


Figure 4. Reaction Window Plot of BATQ-H, ATP (Monomer + Oligomer), and BATQ-H/ATP (Monomer + Oligomer) Blends for 95% Cure.

TABLE 2  
CURE - KINETICS DATA OF BATQ-H/ATP BLENDS

SAMPLE	ACTIVATION ENERGY (KCAL/MOLE)	HEAT OF REACTION (CAL/GRAM)	CALCULATED MOLECULAR WEIGHT (G/MOLE)
BATQ-H	19.759	43.10±2.8	1546
90/10 BATQH/ATP (MONOMER)	21.108	59.16±2.6	1124
80/20 BATQH/ATP (MONOMER)	21.421	79.9±3.2	832
ATP MONOMER	18.067	215.17±12.8	310
90/10 BATQH/ATP MONOMER + OLIGOMER	19.820	50.82±5.9	1308
80/20 BATQH/ATP MONOMER + OLIGOMER	21.266	67.85±5.5	980
ATP MONOMER + OLIGOMER	22.425	193.74±8.2	343

$\Delta H$  FOR ATP (MONOMER) = 66.65 KCAL/MOLE



#### 4. CURE BEHAVIOR

The time of vitrification data for BATQ-H and ATP blends is listed in Table 3 and plotted in Figure 5. It can be seen from this figure that at specific temperatures BATQ-H/ATP blends augment the time available for processing in comparison to BATQ-H alone. Additionally, these vitrification curves for blends extend towards lower temperatures and higher vitrification time. The cure phase diagram indicates that lower temperatures and greater time become available for processing the blended BATQ-H. The improvement in flow behavior of blends is discussed in the following section.

#### 5. VISCOSITY MEASUREMENTS

The flow behavior of BATQ-H and blends is compared by measuring their complex viscosities, isothermally as a function of time. The viscosity data plots obtained from Rheometrics runs are grouped according to the blends. The complex viscosities vs. time data at various temperatures are shown in Figures 6, 7, 8, 9, and 10. Figure 6 shows data for both BATQ-H alone and 90 BATQ-H/10 ATP (monomer only). The effects of the addition of ATP as diluent to BATQ-H are rather obvious. The complex viscosity of BATQ-H at 190°C starts at  $10^5$  poise and builds up to  $4 \times 10^5$  poise in ten minutes. The complex viscosity of BATQ-H at 210°C starts at  $4 \times 10^3$  poise and builds up to  $1.5 \times 10^5$  in 14 minutes. By raising the cure temperature to 210°C, flow of BATQ is increased as evident by lowered viscosity. However, addition of only 10% monomer ATP by weight increase the flow significantly and provides additional curing/processing time. For instance, complex viscosity of 90 BATQ-H/10 ATP at 195°C starts at  $1.4 \times 10^2$  as opposed to  $1.4 \times 10^5$  poise for BATQ-H at 190°C and the time available for processing increases by 30 minutes to 40 minutes.

On comparing 90 BATQ-H/10 ATP blends containing ATP (monomer + oligomer) (Figure 8) with 90/10 blends containing ATP (monomer only) shows that the oligomer content in ATP raises the initial viscosity by a decade which in turn reduces the flow characteristics of these blends. Minor differences in time to vitrification have also been found between these two blends. The blend with ATP (monomer + oligomer) takes somewhat longer

TABLE 3

VITRIFICATION TIMES ( $t_{vit}$ ) FOR BATQ-H AND  
BATQ-H/ATP BLENDS AT VARIOUS TEMPERATURES

<u>COMPOSITION</u>	<u>TEMPERATURE (°C)</u>	<u>T<sub>VIT</sub>(SECS)</u>
BATQ-H	210	1600
BATQ-H	230	1400
BATQ-H	250	1080
BATQ-H	270	950
BATQ-H	290	840
90 BATQ-H/10 ATP (monomer)	175	4500
90 BATQ-H/10 ATP (monomer)	190	3000
90 BATQ-H/10 ATP (monomer)	210	1850
80 BATQ-H/20 ATP (monomer)	175	6200
80 BATQ-H/20 ATP (monomer)	190	3360
80 BATQ-H/20 ATP (monomer)	210	1980
90 BATQ-H/10 ATP (monomer+oligomer)	175	5300
90 BATQ-H/10 ATP (monomer+oligomer)	190	3100
90 BATQ-H/10 ATP (monomer+oligomer)	210	2150
90 BATQ-H/10 ATP (monomer+oligomer)	240	1200
80 BATQ-H/20 ATP (monomer+oligomer)	175°C	7000
80 BATQ-H/20 ATP (monomer+oligomer)	190°C	4000
80 BATQ-H/20 ATP (monomer+oligomer)	210	2100
80 BATQ-H/20 ATP (monomer+oligomer)	240	1260

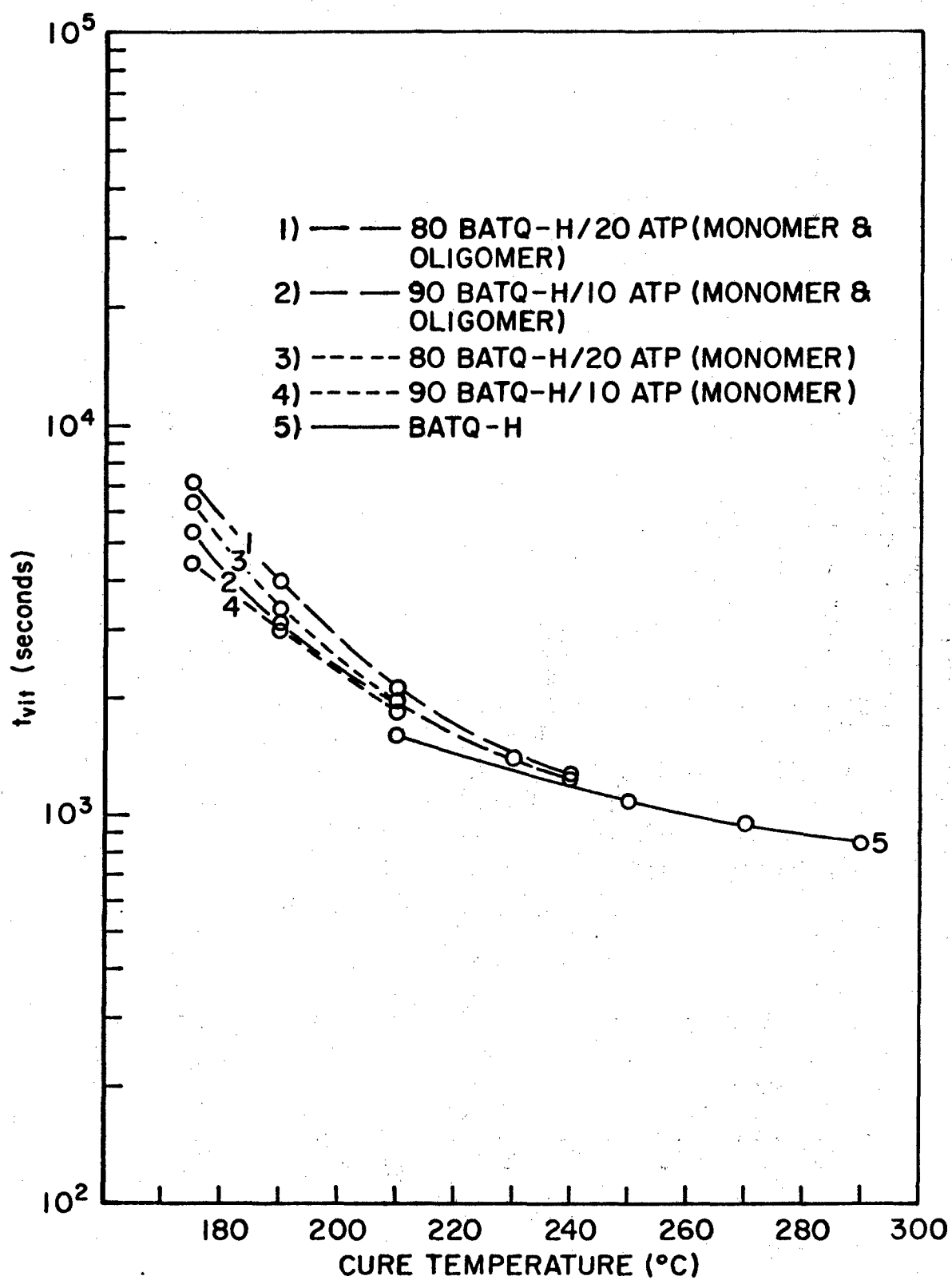


Figure 5. Cure-Phase Diagram for BATQ-H and BATQ-H/ATP Blends.

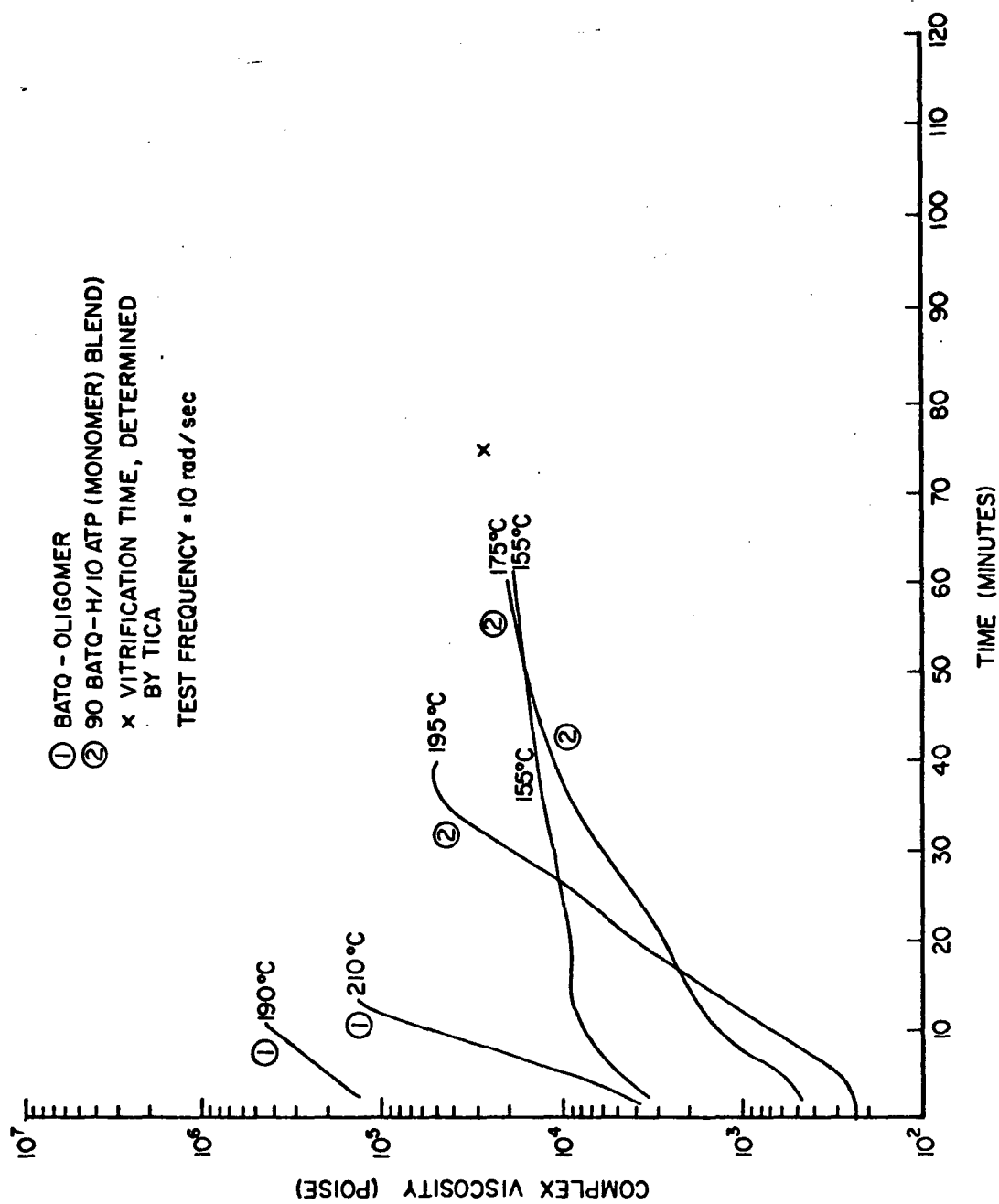


Figure 6. Complex Viscosity vs. Time Plot for BATQ-H and 90 BATQ-H/10 ATP (Mono) Blends. Test Freq. 10 rad/sec.

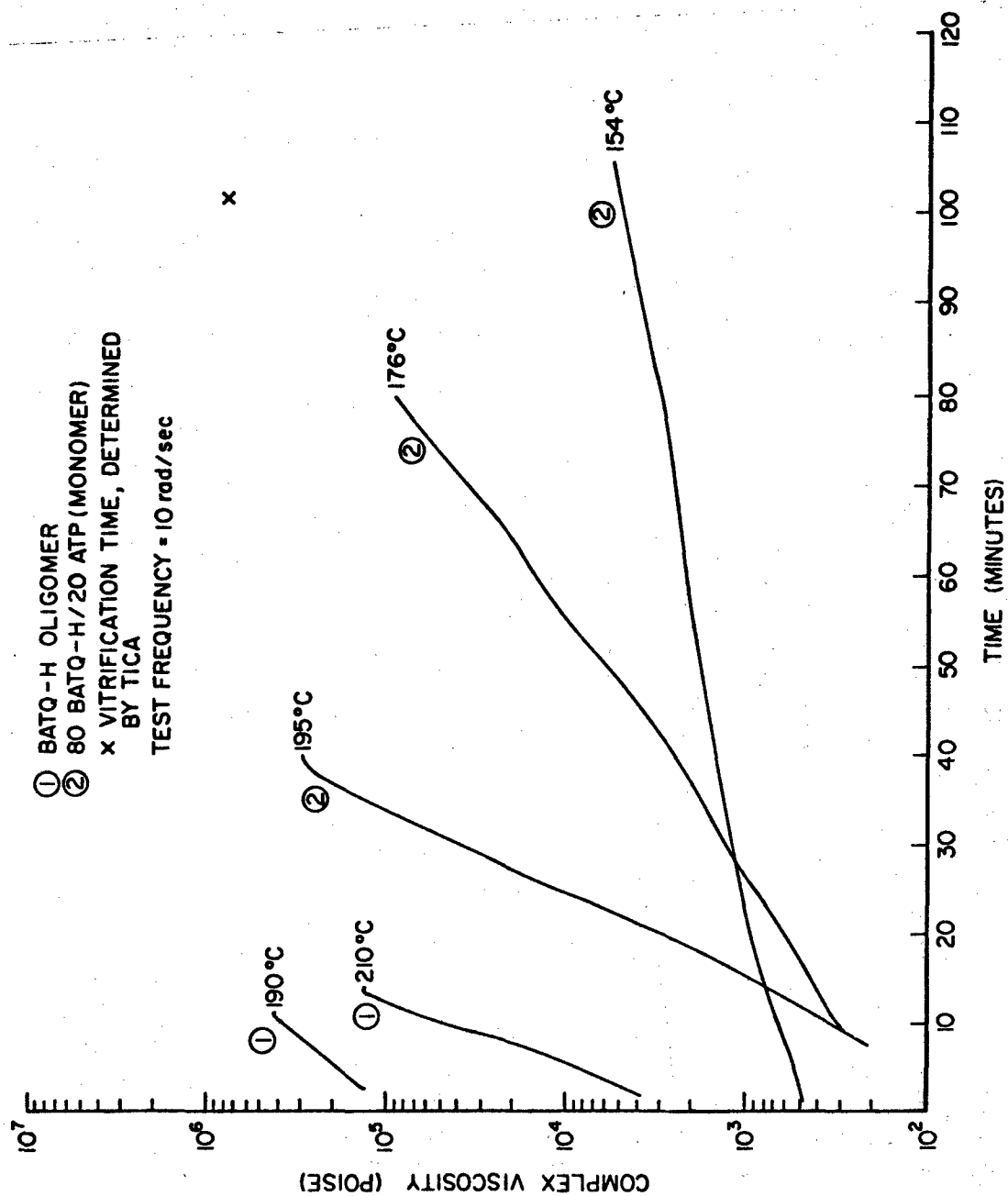


Figure 7. Complex Viscosity vs. Time Plot for BATQ-H and 80 BATQ-H/20 ATP (Mono) Blends.

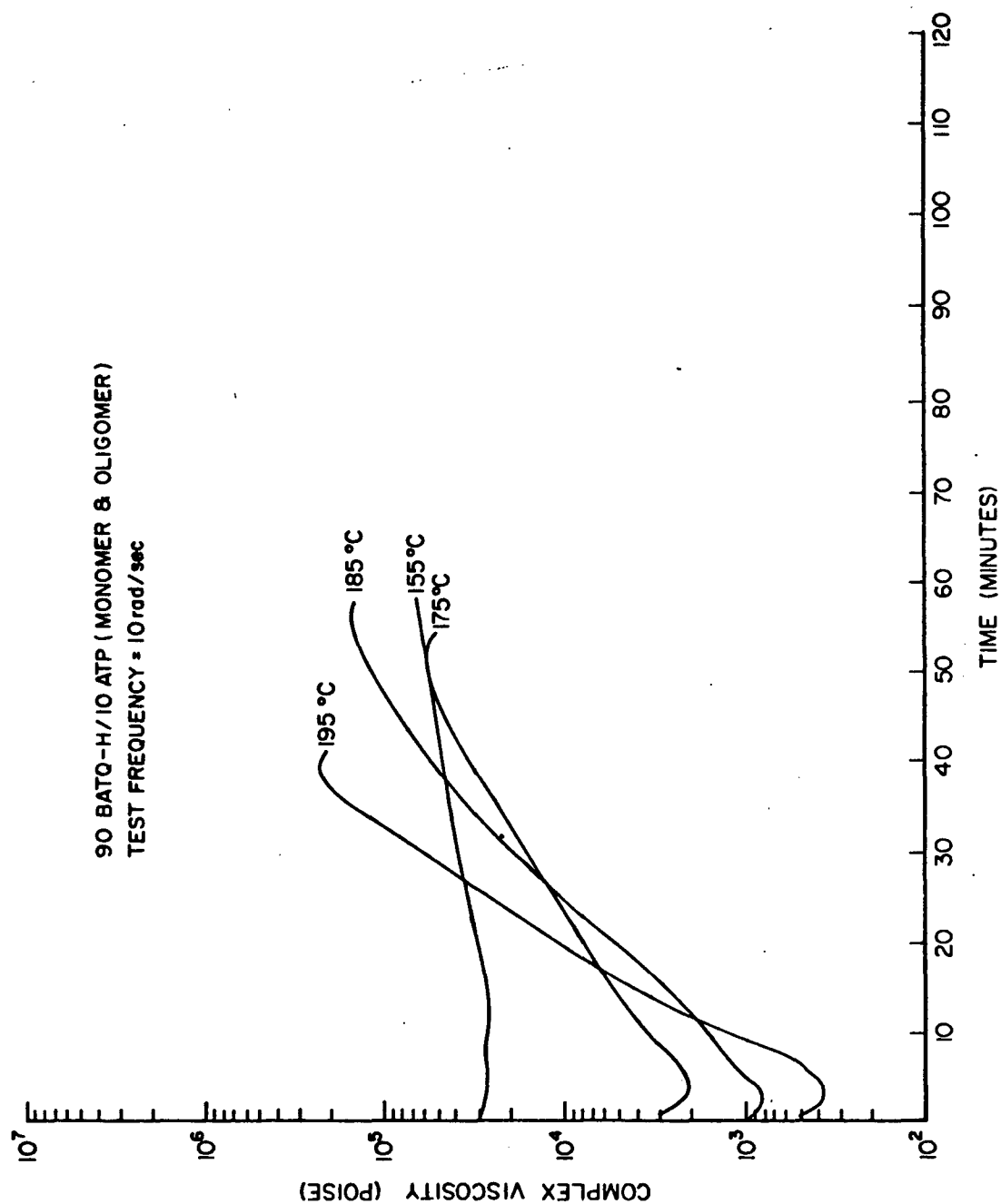


Figure 8. Complex Viscosity vs. Time Plot for 90 BATQ-H/10 ATP (Monomer + Oligomer).

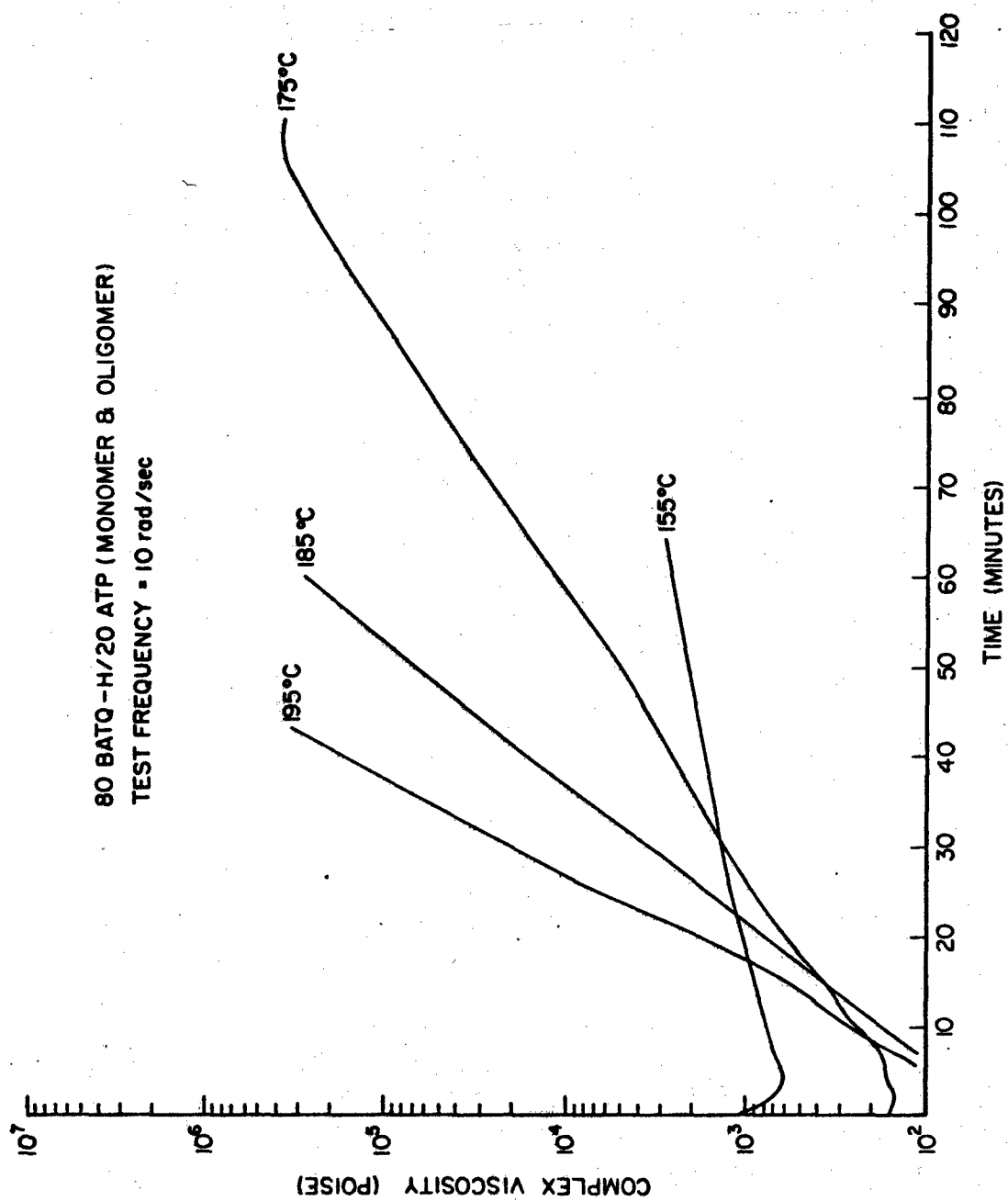


Figure 9. Complex Viscosity vs. Time for 80 BATQ-H/20 ATP (Monomer + Oligomer).

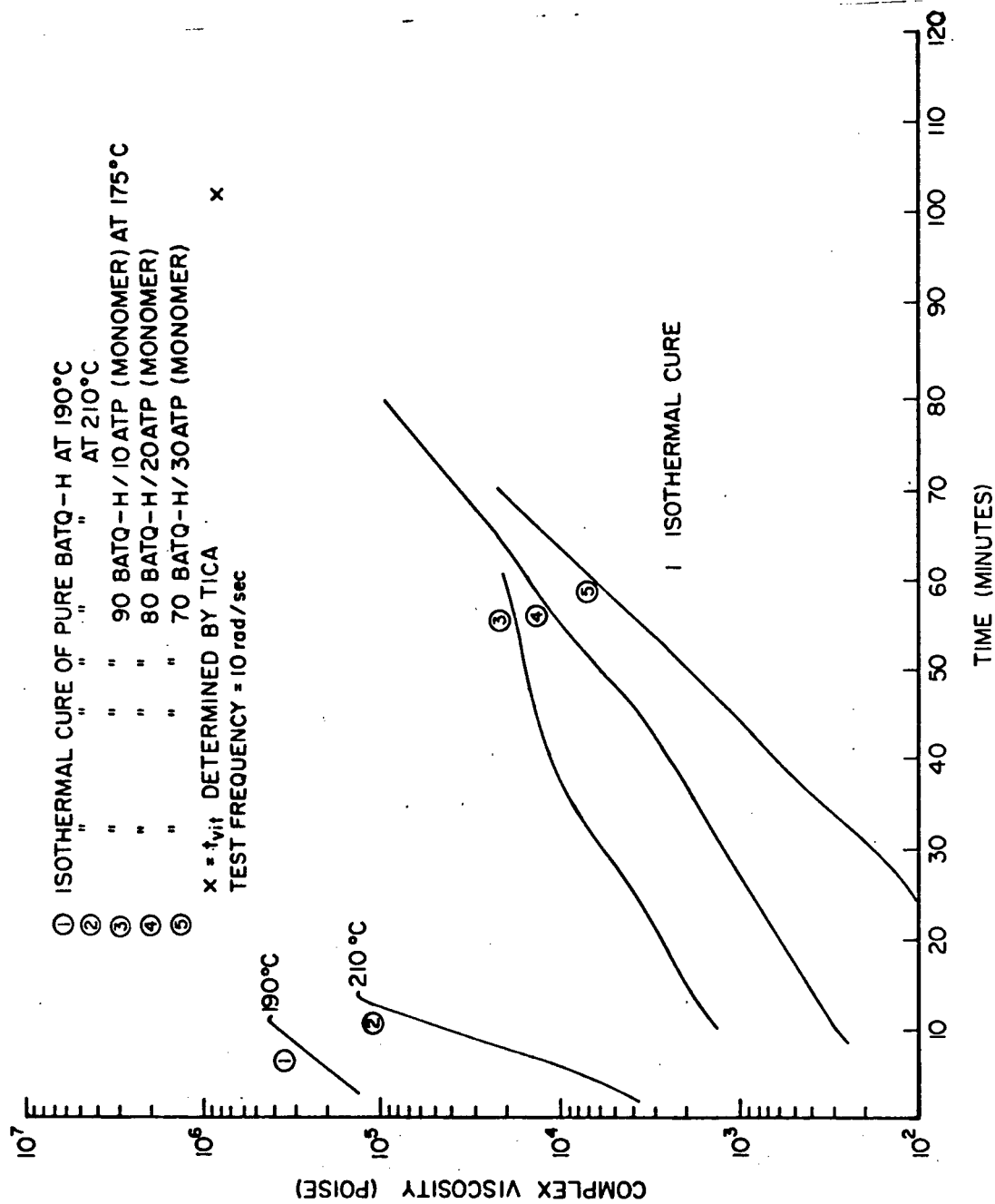


Figure 10. Complex Viscosity vs. Time for 90 BATQ-H/10 ATP, 80 BATQ-H/20 ATP and 70 BATQ-H/30 ATP (ATP Contains Monomer Only in These Blends).



time (ranging from 100-800 seconds at different temperatures) to vitrify than the blend with ATP (monomer). This observation correlates well with our calculated number average molecular weights of blends discussed earlier. The calculated molecular weights of blends with ATP containing oligomer is higher than the blends with ATP containing only monomer. The higher molecular weight oligomers will, therefore, have higher viscosities and longer time to vitrification.

Another point which may be made about the vitrification time ( $t_{vit}$ ) is that although it can be measured using a TICA sample, viscosities of blends close to vitrification during the cure process can not be measured by using parallel plate on the Rheometrics instrument. This is evident from the data obtained from 90/10 blend. The  $t_{vit}$  for 90 BATQ-H/10 ATP (monomer) is 4500 seconds as determined isothermally at 175°C on a TICA sample. Figure 6 shows the viscosity vs. time plot for the same blend obtained isothermally at 175°C using parallel plates. This  $t_{vit}$  of 4500 seconds is well beyond the time period up to which the viscosities have been measured. Therefore, high viscosities of polymers close to their vitrification are beyond the range of the Rheometrics instrument.

Figure 7 shows complex viscosities vs. time for BATQ-H and 80 BATQ-H/20 ATP (mono) blends at various temperatures. Again, it is evident that blending of ATP in BATQ-H improves the cure behavior of BATQ-H. The complex viscosities of BATQ-H start at  $1 \times 10^5$  poise at 190°C and  $3 \times 10^3$  poise at 210°C. At both temperatures, the viscosities build up rapidly (in less than 15 minutes). The improvement in cure behavior of blends is obvious through the display of starting viscosities of 1 to  $4 \times 10^2$  poise at 154, 176 and 195°C. At 195°C, it takes about 40 minutes to reach a viscosity level equalling that of BATQ-H at 190°C. The rate of curing of the blends is even slower at 175°C and it takes up to 80 minutes before viscosities equal that of BATQ-H at 190°C. The temperature of 156°C is not suitable to cure the blends because  $T_{poly}$  onset for blends is above 170°C.

Figure 9 shows the complex viscosity vs. time data for 80 BATQ-H/20 ATP (monomer + oligomer). The complex viscosities of these blends at 175, 185, and 195°C start at  $1 \times 10^2$  poise. The complex viscosity of the blend at 155°C is about  $7 \times 10^2$  poise. As discussed previously 155°C is not a good temperature for processing since it is before  $T_{poly}$  onset and consequently apt to take a long time before any significant cure would take place.

Comparison of Figures 7 and 9 show that 80/20 blends with ATP containing monomer and oligomer cure only at a slightly slower rate than the 80/20 blends with ATP containing monomer. The  $t_{vit}$  of 80/20 blend containing ATP (monomer + oligomer) are 120 and 800 seconds higher than 80/20 blend with ATP (monomer). The real differences between the curves in Figures 7 and 9 are rather small. However, significant differences in the cure behavior of BATQ-H and 80 BATQ-H/20 ATP blend is observable, the latter providing increased flow and greater processing time.

Figure 10 shows complex viscosity vs. time plots for BATQ-H, 90 BATQ-H/10 ATP, 80 BATQ-H/20 ATP, and 70 BATQ-H/30 ATP<sup>1</sup>. It is very clear from these plots that blends of BATQ-H/ATP do provide better processing parameters than BATQ-H oligomer by itself.

## 6. PROPERTIES OF CURED BATQ-H/ATP BLENDS

The glass transition temperature data for BATQ-H/ATP blends have been obtained in both uncured and cured form. The  $T_g$  data of uncured blends presented in Table 1 show single glass transition temperature peaks indicative of compatibility between these two oligomers. The 90 BATQ-H/10 ATP (monomer + oligomer) blend on a TICA sample cured to  $t_{vit}$  at 190°C, quenched and postcured isothermally at 380°C for one hour, shows (Figure 11) the out-of-phase component maximum at 325°C. On scanning above the  $T_g$  (up to 375°C) and then scanning down in temperature,

<sup>1</sup>The 70 BATQ-H/30 ATP blends were prepared by dissolving them in a common solvent chloroform, followed by solvent removal under vacuum and drying at 100°C. The BATQ-H used was Gulf-scaled up batch and the ATP was pure monomer.

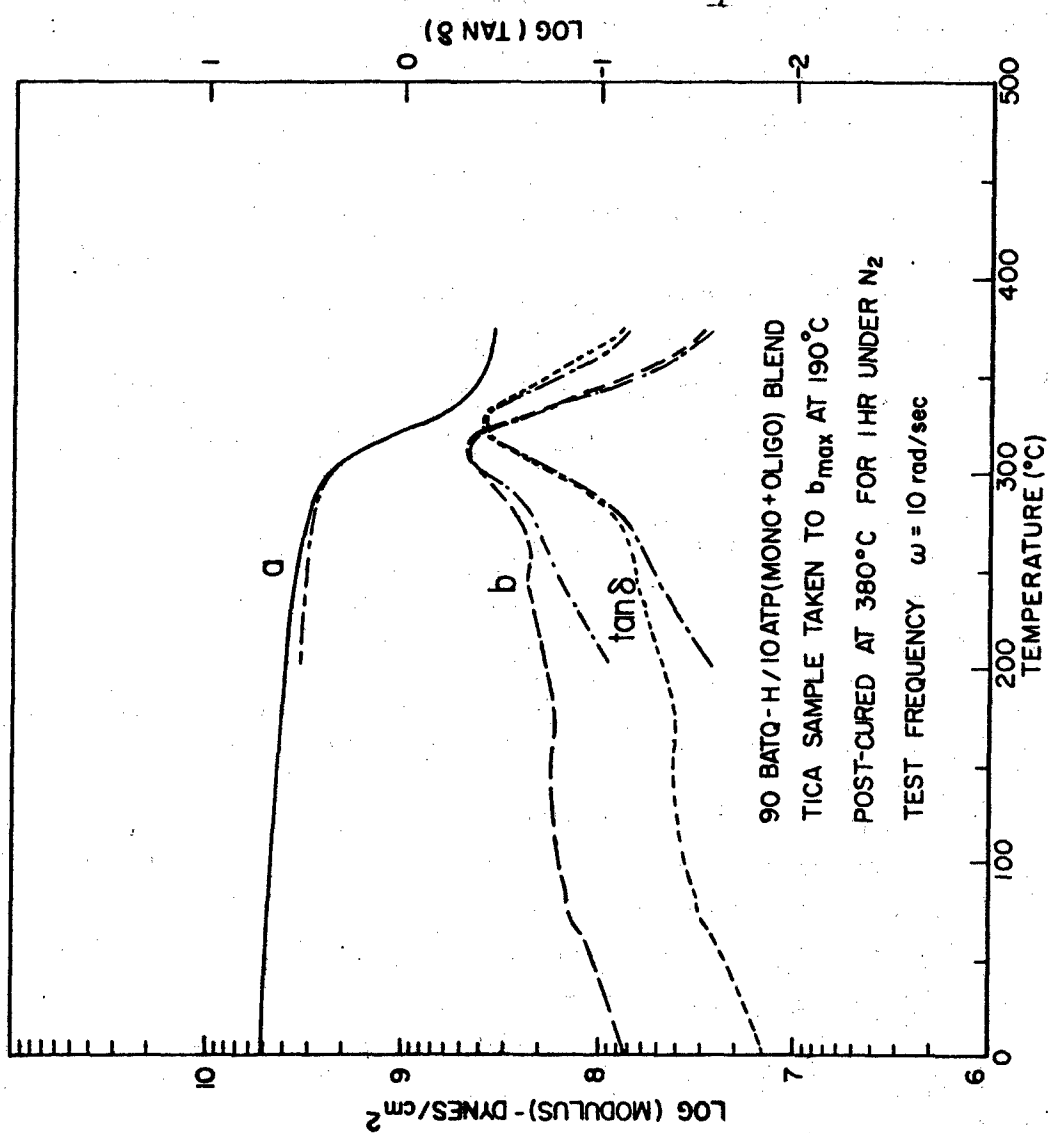


Figure 11. a ( $G'$ ), b ( $G''$ ), Tan  $\delta$  vs. Temperature Plot for 90 BATQ-H/10 ATP (Monomer + Oligomer) Blends.

no change is observed in the  $T_g$  of the blend, which remains at  $325^\circ\text{C}$ . There are also no associated changes in the modulus (in-phase component) while scanning the TICA sample in the cooling mode. Therefore, the  $T_g$  of this blend is the  $T_{g\infty}$  or the  $T_g$  of "fully cured" blend.

Figure 12 shows the plot obtained for 90 BATQ-H/10 ATP (monomer + oligomer) taken to  $t_{vit}$  at  $210^\circ\text{C}$  and postcured for one hour at  $380^\circ\text{C}$  as in case of the above sample. The  $T_g$  of this blend is found to be  $330^\circ\text{C}$  (determined by the out-of-phase component maximum). Again, there is no change/increase in the  $T_g$  of the blend due to scanning above the  $T_g$ . Therefore, this blend also shows a  $T_{g\infty}$  at  $330^\circ\text{C}$ .

The 80 BATQ-H/20 ATP (monomer + oligomer) blends taken to be maximum at  $190^\circ\text{C}$  and  $210^\circ\text{C}$  followed by postcuring at  $380^\circ\text{C}$ , identical to 90 BATQ-H/10 ATP blends described previously, show  $T_{g\infty}$  of  $330^\circ\text{C}$  in both cases. The  $a$  ( $G'$ ),  $b$  ( $G''$ ), and  $\tan \delta$  plots for these blends are shown in Figures 13 and 14.

The  $T_g$ s of 90 BATQ-H/10 ATP cured blends are identical to the  $T_g$  of BATQ-H by itself, determined by DSC after having cured the sample at  $280^\circ\text{C}$  for six hours (Reference 1). Thus, addition of ATP to BATQ-H improves the flow characteristics and other processing parameters while maintaining the high  $T_g$ s desired from these cross-linked thermosets.

Figures 11-14 also show the  $a$  in-phase component which are proportional to the dynamic shear storage moduli. The initial values of which range between  $2.5 \times 10^9$  and  $2 \times 10^{10}$  dynes/cm<sup>2</sup>. For the cured blends, the storage moduli begin to drop past  $275^\circ\text{C}$  making it as the upper temperature limit for end-use applications.

## 7. DENSITY RESULTS

The density of ATP in the uncured state is  $1.1650$  g/ml at  $23^\circ\text{C}$ . The density of cured ATP (cured at  $280^\circ\text{C}$  for two hours), is  $1.2625 \pm 0.0025$  g/ml indicating cross-linked structure. The density of cured 80 BATQ-H/20 ATP (monomer) blend is found to be  $1.2125 \pm 0.0025$  g/ml which is somewhat less than the density of cured ATP indicating higher cross-link density of cured ATP as compared to that of cured BATQ-H.

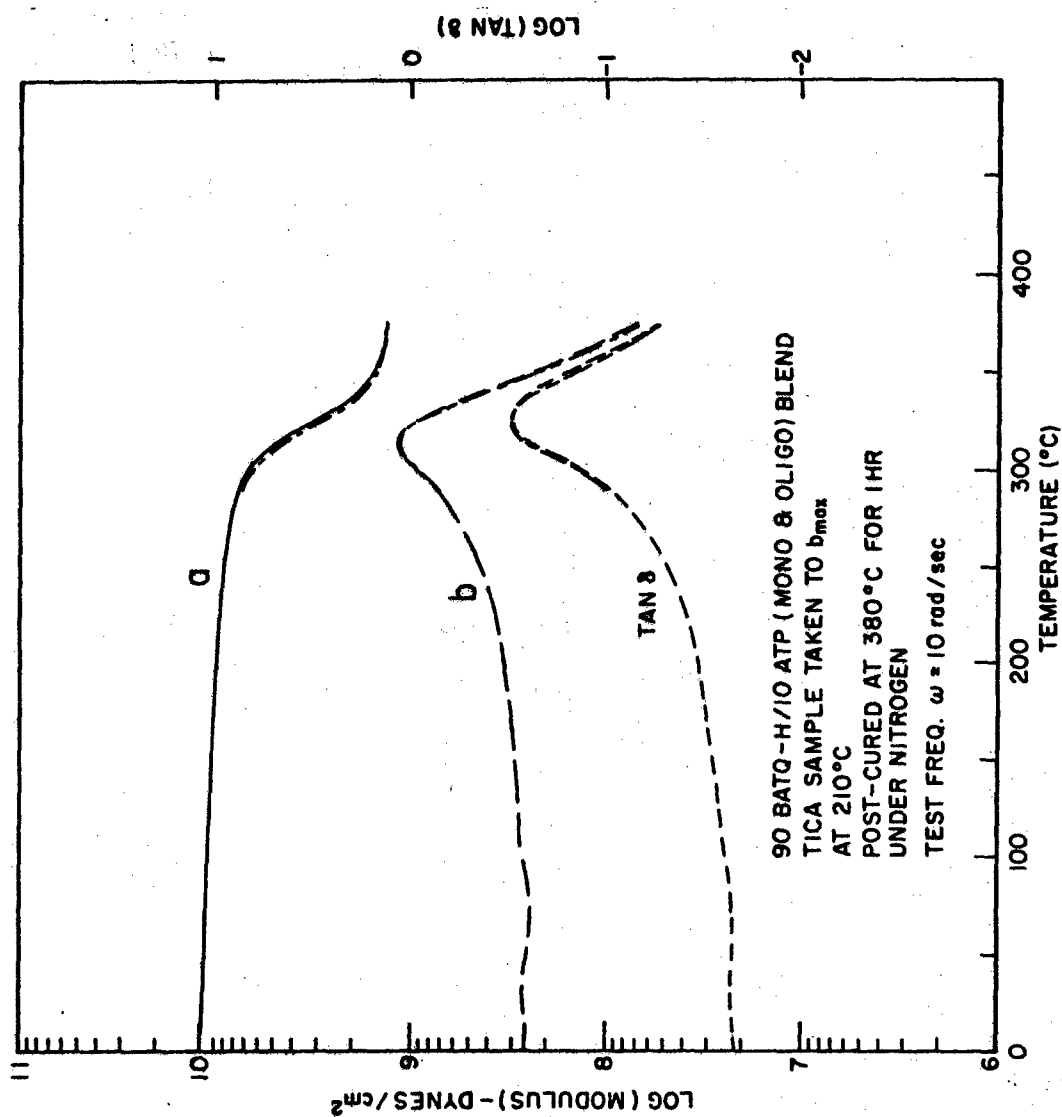


Figure 12. a ( $G'$ ), b ( $G''$ ), Tan  $\delta$  vs. Temperature Plot for 90 BATQ-H/10 ATP (Monomer + Oligomer) Blends.

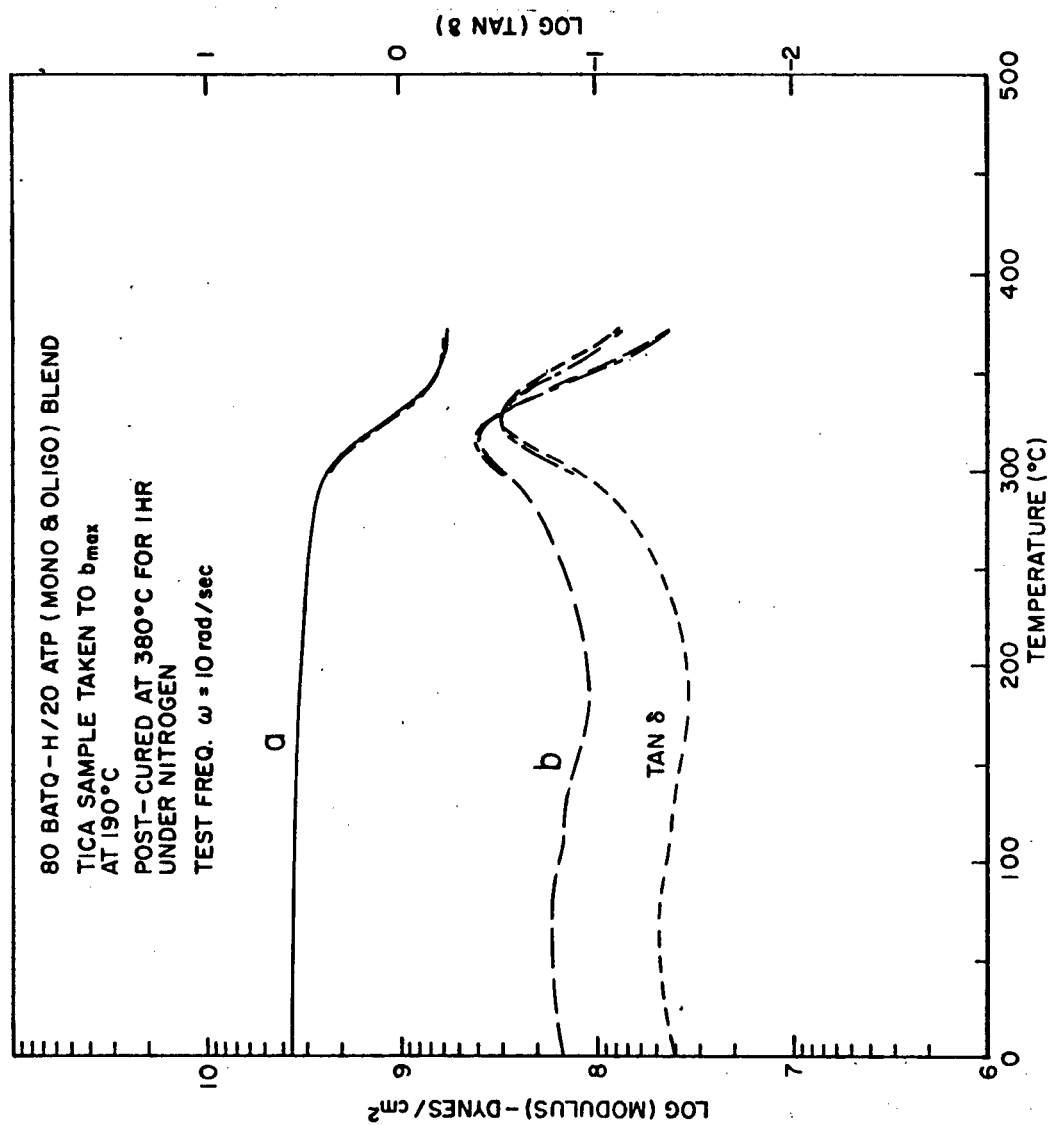


Figure 13. a ( $G'$ ), b ( $G''$ ), Tan  $\delta$  vs. Temperature Plot for 80 BATQ-H/20 ATP (Monomer + Oligomer) Blends.

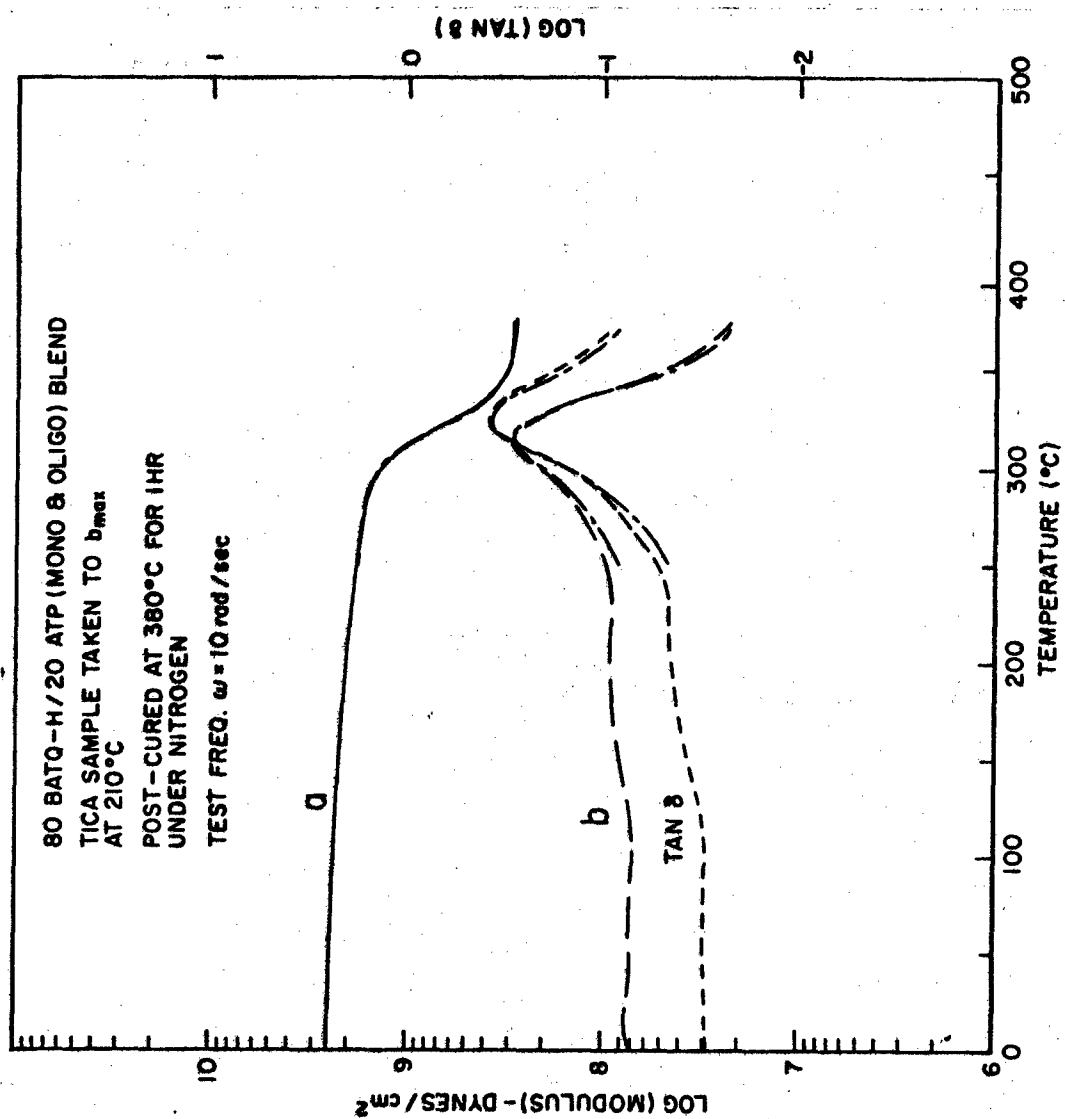


Figure 14. a ( $G'$ ), b ( $G''$ ), Tan  $\delta$  vs. Temperature Plot for 80 BATQ-H/20 ATP (Monomer + Oligomer) Blends.

## SECTION IV

### CONCLUSIONS

This work was performed to demonstrate the improvement in the processability of high-temperature thermoset oligomer BATQ-H by blending it with small amounts of low-molecular weight reactive diluent (acetylene terminated phenoxy). Additionally, the influence of reactive diluent on thermal and mechanical properties of blends was studied.

These studies have shown that high-temperature thermoset oligomer BATQ-H can be processed by the addition of reactive diluents in 10 and 20 weight percent composition with BATQ-H. The oligomers appear to form compatible blends based on thermoanalytical data.

The dynamic viscosities of blends are lowered due to addition of diluent and therefore greater time is available for processing the oligomers at different temperatures.

Blending of ATP containing only monomer versus ATP containing mixture of monomer and oligomers and other impurities does not cause any significant difference in processability of the oligomer.

The glass transition temperatures of cured BATQ-H/ATP blends indicating  $T_g^\infty$  in all cases, are 325°C; which are identical to the  $T_g$  of cured BATQ-H by itself. Therefore, blending BATQ-H with an AT diluent does not change its  $T_g$  (in the "fully cured") state.

The dynamic storage shear moduli of cured blends determined by TICA samples suggest upper end-use temperature to be 275°C, past which the dynamic storage moduli begin to drop.



REFERENCES

1. F. L. Hedberg and F. E. Arnold, AFML-TR-78-142, (December 1978).
2. R. F. Kovar and F. E. Arnold, Sci, Adv. Mat's and Process Eng. Ser. 8, 106 (1976).
3. B. A. Reinhardt and F. E. Arnold, AFML-TR-80-4012.
4. J. M. Pickard, E. G. Jones and I. J. Goldfarb, Polymer Preprints, 20, (2), 370 (1979).
5. R. L. Elliot, B. I. Hauber and S. H. Nearing, AFML-TR-69-326.
6. C. Y. C. Lee, I. J. Goldfarb and J. D. Henes, AFWAL-TR-80-4159.